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Decay of Multiple Spin Echoes in Dipolar Solids

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lattices increases a few degrees below T_c. Critical superparamagnetism cannot therefore be the cause of the $\beta = \frac{1}{2}$ exponent found near T_c in magnetization measurements.

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In this paper we derive a general expression describing the evolution of the transverse nuclear-spin magnetization for the Ostroff–Waugh multiple-spin-echo experiment in dipolar solids. Our approach consists of expressing the formula for the magnetization at even echoes in a form resembling an ordinary time-correlation function, and then evaluating this quantity by means of Zwanzig's projection-operator technique. For long times, we show that under certain conditions the echo envelope decays exponentially, in agreement with experiment. A general expression is obtained for the time constant T^* associated with the decay. This result may be used to generate an expansion of $1/T^*$ in powers of the cycle time t_c, but there are experimental indications that this expansion is not legitimate and that more complicated t_c dependences can arise. In the case when higher-order correlations decay much more rapidly than lower-order ones, our result reduces to $1/T^* = A t_c^4 \tau_c^0 (t_c)$, where A is a quantity related to the sixth moment of the magnetization and $\tau_c^0 (t_c)$ is a characteristic correlation time associated with decay of the lowest-order correlation function which enters the problem. The t_c dependence of T^* is then determined by the behavior of $\tau_c^0 (t_c)$, and is in general more complex than the proportionality between $1/T^*$ and t_c^5 found previously. This previous result emerges in the case when $\tau_c^0 (t_c) = t_c$. Available experimental results suggest that $1/T^*$ is in general a nonanalytic function of t_c, as indicated by the observed proportionality between $1/T^*$ and t_c for Teflon and $KAsF_6$. Further experimental results are needed to clarify the nature of this nonanalytic behavior.

I. INTRODUCTION

It was reported[1,2] that a periodic train of 90° rf pulses can greatly prolong the decay of transverse nuclear spin magnetization in dipolar solids. The effect is observed as a train of multiple spin echoes analogous to (but quite different in character from) the familiar "classical" spin echoes first observed by Hahn.[3] A detailed analysis of this effect, including the dependence of the decay time T^* for the echo envelope upon the pulse spacing, was given by Waugh and Wang.[4] The pulse sequence which gives rise to the effect may be represented symbolically as P_x, τ, P_y, $(2\tau, P_y)_n$, where

P_α $(\alpha = x, y)$ denotes a 90° pulse along the α axis of a reference frame rotating at the Larmor frequency ω_0 $(= \gamma H_0)$. The first pulse P_x serves merely to establish a suitable initial condition for the remainder of the sequence. This pulse is followed, after a time τ, by a train of n P_y pulses $(n \sim 10^3)$ spaced apart by a time 2τ.

The free induction decay following a single P_x pulse in a dipolar solid decays nonexponentially to zero on a time scale T_2 (T_2 is the normal transverse relaxation time). However, the echo train induced by the action of the subsequent P_y pulses persists for times several orders of magnitude longer than T_2.[1,2,4] In fact, by reducing the pulse

spacing the time constant T^* characterizing the decay of the echo envelope can be made to approach $T_{1\rho}$, the spin-lattice relaxation time in the rotating frame.[1,4]

As mentioned above, the multiple spin echoes under consideration here are of a completely different character from the ordinary spin echoes used to recover decay caused by static inhomogeneous interactions. These ordinary spin echoes are normally observed in liquids, and depend for their occurrence upon a distribution in Larmor frequencies due to such causes as magnetic field inhomogeneities, quadrupole coupling, dipolar coupling to nonresonant spins, and so on. In contrast, the multiple spin echoes induced in dipolar solids by a train of $90°$ pulses are more complex in nature, being governed by the manner in which the N-body magnetic-dipole–dipole interactions (and other terms in the spin Hamiltonian) transform under the action of the pulses.

By exploiting the symmetry which the dipolar Hamiltonian exhibits under the influence of two successive $90°$ pulses, Waugh and Wang[4] were able to show that for short times (i.e., $n\tau \approx T_2$) the decay of the echo envelope is proportional to n^2. However, at long times (i.e., $n\tau \gg T_2$) the echo envelope is observed to decay exponentially in a variety of samples.[4-7] It is therefore clear that the longer-time behavior cannot properly be accounted for by a naive projection of the short-time behavior, for such a projection would imply a Gaussian rather than an exponential decay. Recognizing this difficulty, Waugh and Wang attempted to calculate the long-time behavior of the echo envelope by combining the calculated decay of the magnetization after one cycle ($n = 2$) with an *Ansatz* (similar in spirit to the familiar *Stosszahlansatz* of Boltzmann) concerning the manner in which this decay accumulates at long times. According to this argument, the time constant T^* which characterizes the exponential decay of the echo envelope should be proportional to τ^{-5}. It is of interest to note that in at least two samples (CaF_2 and K_2SiF_6) T^* is observed to have precisely this τ dependence.[4] The agreement between theory and experiment in the case of CaF_2 was subsequently confirmed even more strongly by Mansfield and Ware.[6]

However, the proportionality of T^* to τ^{-5} for this experiment is by no means universal. Experimental data for Teflon and $KAsF_6$ indicate a proportionality between T^* and τ^{-1}.[5] In other samples still different dependences of T^* upon τ are observed. We mention in particular the recent work of Mansfield, Richards, and Ware[7] (MRW) on solid samples containing more than one spin species. MRW report that their experimental data cannot be explained on the basis of the simple *ad*

hoc argument used by Waugh and Wang. In order to account for their experimental results, MRW present a modification of Anderson's theory of spectral-line narrowing in solids.[8] Although they are able to fit their observations into the framework of this theory, their work does not appear to clarify substantially the manner in which different dependences of T^* upon τ might manifest themselves in different circumstances.

The purpose of the present paper is to derive a general expression for the decay time T^*. In principle, this expression contains the full dependence of T^* upon τ. In this paper we shall restrict attention to the case in which only a single spin species is present. The generalization to several spin species will be considered in a subsequent publication. Our method of approach is to cast the problem into a form which resembles an ordinary time-correlation-function calculation, and then to evaluate the resulting expression using the projection-operator technique developed by Zwanzig.[9] Our results indicate that T^* may exhibit a variety of different τ dependences depending upon the circumstances. One possibility is that $1/T^*$ may be expanded in powers of τ. The coefficients in this expansion may easily be generated from our basic result for T^*. Unfortunately, however, there are experimental indications that such an expansion is frequently not legitimate. The reason for this is unclear; it may be that experimentally accessible values of τ are not "small enough" in the required sense, or it may be due to some inherent nonanalyticity in the problem. In any event, if the expansion of $1/T^*$ in powers of τ is *not* legitimate, then the manner in which T^* depends upon τ is critically dependent upon the properties of the correlation function which appears in the expression for T^* [see Eq. (34)]. This correlation function is of course too complicated to permit a direct evaluation; the best that can be done is to consider several possible forms for it and examine the τ dependence to which each gives rise. We do this in connection with our discussions of experimental data, and indicate how the original τ^{-5} dependence, as well as other τ dependences, may arise.

Although our main concern in this paper is with the P_x, τ, P_y, $(2\tau, P_y)_n$ pulse sequence, our method may equally well be applied to analyze the decay times for other pulse sequences. It will be remembered that the principal significance of the prolonged decay time in the Ostroff–Waugh experiment[1] was the line narrowing which it implied in frequency space. Motivated by the possibility this suggested for accomplishing "high-resolution" NMR in solids, Waugh and co-workers[10-15] soon discovered that the decay of the magnetization in a wide class of multiple-pulse experiments could

be simply understood by introducing the concept of an "average Hamiltonian" which is determined by the symmetry properties of the true Hamiltonian under the pulse transformations. Once this concept became clearly understood, it became possible to design pulse sequences specifically to suppress the dipole-dipole interactions, enabling the structure associated with more interesting interactions (such as chemical shifts) to be resolved. A number of experiments of this type were quickly proposed and successfully performed.[10-17]

Although the line-narrowing capabilities of such experiments can be analyzed in terms of the average Hamiltonian and its higher-order correction terms,[13] we feel that the approach of this paper may have some complementary usefulness in this regard. In fact, our work may be regarded as a natural extension of that of Waugh and co-workers. They have considered in great detail the form of the average Hamiltonian and its low-order correction terms for a variety of multiple-pulse experiments. Our approach goes one step further and considers explicitly the corresponding time decay of the echo envelope. In order that our work may be applicable to a variety of multiple-pulse experiments, we present the basic theory in a form which is independent of the particular pulse sequence under consideration (so long as it is cyclic). We then specialize our results to the case of particular interest in this paper.

II. THEORY

1. *Evolution of the transverse spin magnetization under the action of a train of rf pulses.* We consider the evolution of a system under the influence of a time-dependent Hamiltonian $\mathcal{3C}(t)$. This evolution is most compactly described in terms of the density operator $\rho(t)$, which satisfies the von Neumann–Liouville equation

$$i\hbar \frac{\partial \rho}{\partial t} = [\mathcal{3C}(t), \rho(t)] . \tag{1}$$

In the rotating-coordinate frame, the time dependence of $\mathcal{3C}(t)$ is due to a cyclic train of rf pulses applied in the plane normal to the static magnetic field. (Nonsecular terms oscillating at multiples of the Larmor frequency also arise when the transformation to the rotating frame is made, but their effects are unimportant for our purposes so these terms are neglected.) Also contained in $\mathcal{3C}(t)$ is a time-independent internal Hamiltonian $\mathcal{3C}_{\text{int}}$. In this paper we shall neglect spin-lattice relaxation and consider the lattice to be rigid. In this case, $\mathcal{3C}_{\text{int}}$ is a time-independent function of spin variables. It also depends, of course, on lattice variables (such as the distance r_{ij} between spins i and j), but these are present only as constant parameters. Typical contributions to $\mathcal{3C}_{\text{int}}$ for solids in-

clude dipole-dipole interactions, scalar couplings, chemical shifts, and so on. In conventional NMR experiments in solids, the dipole-dipole interactions give rise to a broad, featureless spectrum, making it impossible to extract information concerning the other interactions. Multiple-pulse experiments are of interest because they make possible the suppression of the dipole-dipole interactions, thereby allowing the resolution of spectral details associated with the other interactions.

In general, the solution to Eq. (1) involves a time-ordering operator,[13] which is necessary to make proper allowance for the interference between the internal Hamiltonian and the specific rf pulse sequence used in the experiment. We shall consider the situation in which the rf pulse field, when present, is much greater than the internal dipolar field. This situation is readily achieved in multiple-pulse experiments. In this case the effect of a pulse is essentially that of a δ function; the pulse may then be represented by a rotation operator in the rotating frame. Our specific concern in this paper is with 90° pulses; the corresponding rotation operator simply effects a 90° rotation of the spin operators along a predetermined direction in the rotating frame.

Experimentally, of course, the pulses are not really δ functions, and in some cases the effects of finite pulse width become important. Haeberlen and Waugh[13] have showed how to allow for these effects.

Before the application of the rf pulses, the spin system is at equilibrium and is described by the density operator $\rho_{\text{eq}} = Z^{-1} \exp[-\beta(\mathcal{3C}_z + \mathcal{3C}_{\text{int}})]$, where $\mathcal{3C}_z$ is the Zeeman Hamiltonian and Z is the partition function. In the high-temperature approximation, ρ_{eq} can be written

$$\rho_{\text{eq}} \approx (\text{Tr} 1_{\text{op}})^{-1} [1_{\text{op}} - \beta(\mathcal{3C}_z + \mathcal{3C}_{\text{int}})]$$

$$\approx (\text{Tr} 1_{\text{op}})^{-1} [1_{\text{op}} + \beta \hbar \omega_0 I_z] , \tag{2}$$

where $\omega_0 = \gamma H_0$ is the Larmor frequency. The internal Hamiltonian may be neglected in the high-temperature approximation because its contribution is thousands of times smaller than the Zeeman term in the experiments considered here. Now $\text{Tr} 1_{\text{op}} = (2I+1)^N$ is simply a constant, and the unit operator on the right-hand side of Eq. (2) makes no contribution to the magnetization (since angular momentum operators are traceless). Therefore, the useful or significant part of the equilibrium density operator before the rf pulsing is simply proportional to I_z.

In all multiple-pulse experiments, the first 90° pulse P_x serves to prepare a state with nonzero transverse magnetization. After this initial 90° pulse the density operator therefore becomes proportional to I_y. For the purpose of calculating the

transverse magnetization after the ensuing coherent set of pulses, it is convenient to consider I_y as an initial condition: $\rho(0) = I_y$. The subsequent evolution of $\rho(0)$ is then governed by the internal Hamiltonian and the remainder of the rf pulses. Thus, the density operator which describes the free induction decay at a time τ after the first pulse P_x is

$$\rho(\tau) = \mathfrak{D}(\tau) I_y \mathfrak{D}^{-1}(\tau) , \qquad (3)$$

where

$$\mathfrak{D}(\tau) = \exp(-i \mathfrak{K}_{int} \tau) . \qquad (4)$$

In Eq. (4) we have adopted the convention of writing $\mathfrak{K}_{int}$ in units of angular frequency, which is equivalent to setting $\hbar = 1$. This convention will be observed throughout the remainder of this paper.

But instead of observing the free induction decay, we apply another pulse P_1 at a time $\tau = \tau_0$. We then let the system evolve freely for a time τ_1, and then apply another pulse P_2. We continue in this manner until a sequence of N pulses $\{P_1 P_2 \cdots P_N\}$ has been applied, the spacing between successive pulses P_i and P_{i+1} being denoted by τ_i. At a time τ_N after the pulse P_N the density operator has become

$$\rho_N = K I_y K^{-1} , \qquad (5)$$

where

$$K = \mathfrak{D}(\tau_N) P_N \mathfrak{D}(\tau_{N-1}) P_{N-1} \cdots P_1 \mathfrak{D}(\tau_0) . \qquad (6)$$

There exists no simple way of calculating ρ_N for an arbitrary rf pulse sequence with random pulse spacings. However, a considerable simplification results if (a) the pulse sequence is designed in such a way that a set of m successive pulses ($m \ll N$) recovers the original Hamiltonian, i.e.,

$$P_{j+m} \cdots P_{j+1} \mathfrak{K}_{int} P_{j+1}^{-1} \cdots P_{j+m}^{-1} = \mathfrak{K}_{int} ; \qquad (7)$$

(b) the pulse spacings are so adjusted that the pulse sequence becomes periodic in time, each period t_c containing m pulses. Pulse sequences satisfying these conditions are said to be cyclic[10,13]; the period t_c is called the cycle time, and is equal to $\tau_0 + \tau_1 + \cdots + \tau_m$.

If the pulse sequence is cyclic and if N is an integral multiple of m (say $N = nm$), then Eq. (5) reduces to

$$\rho_N(N = nm) = L^n(t_c) I_y L^{-n}(t_c) , \qquad (8)$$

where the one-cycle propagator $L(t_c)$ is given by

$$L(t_c) = \mathfrak{D}(\tau_m) P_m \mathfrak{D}(\tau_{m-1}) \cdots P_1 \mathfrak{D}(\tau_0) . \qquad (9)$$

The y component (in the rotating frame) of the transverse magnetization at the end of the nth pulse cycle is then proportional to

$$\langle I_y(nt_c) \rangle = \mathrm{Tr}[I_y L^n(t_c) I_y L^{-n}(t_c)] . \qquad (10)$$

The one-cycle propagator $L(t_c)$ defined in Eq. (9) can be rewritten in the form[10]

$$L(t_c) = [\mathfrak{D}(\tau_m) \mathfrak{D}_m(\tau_{m-1}) \mathfrak{D}_{m,m-1}(\tau_{m-2}) \cdots$$
$$\times \mathfrak{D}_{m,m-1,\ldots,1}(\tau_0)] (P_m P_{m-1} \cdots P_2 P_1) , \qquad (11)$$

where

$$\mathfrak{D}_{i,j,\ldots}(\tau) = \exp[-i\tau(P_i P_j \cdots \mathfrak{K}_{int} \cdots P_j^{-1} P_i^{-1})] . \qquad (12)$$

Things become simpler if we now restrict attention to cycles such that

$$P_m P_{m-1} \cdots P_2 P_1 f(I) = e^{i\phi} f(I) , \qquad (13)$$

where ϕ is some real number and $f(I)$ is any function of spin variables. Equation (13) is clearly sufficient to guarantee that Eq. (7) is satisfied; it is also necessary if Eq. (7) is to be satisfied for arbitrary $\mathfrak{K}_{int}$, since any operator which commutes with every other operator must be proportional to the unit operator. Now if Eq. (13) is satisfied, then the pulse operators $(P_m P_{m-1} \cdots P_2 P_1)$ in Eq. (11) cancel out when this equation is substituted into either Eq. (8) or (10). For the purpose of calculating $\langle I_y(nt_c) \rangle$, therefore, Eq. (11) may be replaced by

$$L(t_c) = \mathfrak{D}(\tau_m) \mathfrak{D}_m(\tau_{m-1}) \cdots \mathfrak{D}_{m,m-1,\ldots,}(\tau_0) . \qquad (14)$$

It is convenient to define a t_c-dependent effective Hamiltonian $\mathfrak{K}_e(t_c)$ by the equation

$$L(t_c) = \exp[-it_c \mathfrak{K}_e(t_c)] . \qquad (15)$$

Since $L(t_c)$ is unitary, $\mathfrak{K}_e(t_c)$ must be Hermitian. It may be evaluated in series form by means of the Magnus expansion,[13,18,19] which yields

$$\mathfrak{K}_e(t_c) = \overline{\mathfrak{K}} + \sum_{k=1}^{\infty} \overline{\mathfrak{K}}^{(k)}(t_c) , \qquad (16)$$

together with a prescription for determining the quantities $\overline{\mathfrak{K}}$ and $\overline{\mathfrak{K}}^{(k)}(t_c)$. The quantity $\overline{\mathfrak{K}}$ is called the average Hamiltonian; as indicated by our notation it is independent of t_c. If the pulse spacings are fixed fractions of t_c then $\overline{\mathfrak{K}}^{(k)}(t_c) = t_c^k F_k$, where F_k is a Hermitian operator independent of t_c. The expansion in Eq. (16) is therefore simply a power series in t_c. The quantities F_k can be determined either by the Magnus prescription or simply by expanding both Eqs. (14) and (15) in powers of t_c and equating coefficients.

We see from Eqs. (15) and (16) that in the limit $t_c/T_2 \to 0$, $n \to \infty$, and $nt_c = \mathrm{const}$ $L^n(t_c)$ approaches $\exp(-int_0\overline{\mathfrak{K}})$ exactly. Historically,[10] this fact was realized before it became clear how to introduce correction terms which allow for finite t_c. These correction terms are important, however, since the mathematical limit t_c/T_2 is of course not realized in practice. In the present context, these corrections are of vital importance to the calculation of the decay of $\langle I_y(nt_c) \rangle$, since if they were

omitted there would be no decay of the magnetization.[10]

The above development is essentially a capsule summary of what has become known as average Hamiltonian theory. We have included it both in order to make our presentation self-contained and to avoid notational inconsistencies. Since it is probably too condensed to serve as an introduction to the subject, the reader desiring further details is referred to the original sources.[4,10-15]

2. *Exact integral equation for the transverse magnetization.* According to Eq. (15), the n-cycle propagator which develops the system for a time nt_c is simply equal to $\exp[- int_c \mathcal{3C}_e(t_c)]$. Equation (10) therefore becomes

$$\langle I_y(nt_c)\rangle = \mathrm{Tr}\left\{I_y \exp[- int_c \mathcal{3C}_e(t_c)]I_y \exp[int_c \mathcal{3C}_e(t_c)]\right\}. \quad (17)$$

Equation (17) now appears in a form resembling an ordinary time-correlation function. Having put $\langle I_y(nt_c)\rangle$ into this form, we are now in a position to evaluate it using the projection-operator technique introduced into statistical mechanics by Zwanzig.[9] At first there appears to be a problem, because Eq. (17) is valid only for integral values of n; that is, only for times which are an integral multiple of the cycle time t_c. In order to avoid the problems associated with a discrete variable, we simply *define* a continuous function $G(t)$ of the continuous variable t by

$$G(t) \equiv \mathrm{Tr}\{I_y \exp[- it\mathcal{3C}_e(t_c)] I_y \exp[it\mathcal{3C}_e(t_c)]\}$$
$$\equiv \mathrm{Tr}\{I_y I_y(t)\} \equiv \langle I_y I_y(t)\rangle. \quad (18)$$

We then proceed to calculate the evolution of $G(t)$ as t is varied continuously. At the end of the calculation, we can regain $\langle I_y(nt_c)\rangle$ by setting $t = nt_c$ in $G(t)$, i.e., $\langle I_y(nt_c)\rangle = G(nt_c)$. In this manner we can obtain rigorous information about the spin magnetization at integral multiples of the cycle time t_c, even though $G(t)$ does not correspond to the magnetization at other times.

It is, of course, understood that $G(t)$ depends parametrically upon t_c as well as upon t, even though the former dependence has been suppresse for notational convenience. Since we shall calculate $G(t)$ by varying only t, t_c remains constant throughout our development and we need not worry about it.

We first differentiate $I_y(t)$ with respect to t, obtaining

$$\frac{\partial I_y(t)}{\partial t} = i[\mathcal{3C}_e(t_c), I_y(t)] \equiv i\mathcal{L}(t_c)I_y(t), \quad (19)$$

with the initial condition $I_y(0) = I_y$. Equation (19) is formally identical to the Heisenberg equation of motion for the operator I_y in a system whose time-independent Hamiltonian is equal to $\mathcal{3C}_e(t_c)$. We have introduced, in Eq. (19), the Liouville opera-

tor $\mathcal{L}(t_c)$ corresponding to the effective Hamiltonian $\mathcal{3C}_e(t_c)$. $\mathcal{L}(t_c)$ is a superoperator, which yields the commutator $[\mathcal{3C}_e(t_c), A]$ when it operates on any operator A.

We are not really interested in the complete solution to Eq. (19); we want only the component of $I_y(t)$ which is necessary to calculate $G(t)$. Following Zwanzig,[9] we call this component the relevant part of $I_y(t)$ and denote it by $I_1(t)$. This component can be separated out by the use of a projection operator $\mathcal{P}$ defined as follows:

$$\mathcal{P}A = \langle I_y A\rangle \langle I_y^2\rangle^{-1} I_y, \quad (20)$$

where A is any quantum-mechanical operator. It is easy to show from this definition that $\mathcal{P}$ is idempotent, i.e., $\mathcal{P}^2 = \mathcal{P}$. We therefore write

$$I_1(t) = \mathcal{P}I_y(t) = \langle I_y I_y(t)\rangle \langle I_y^2\rangle^{-1} I_y. \quad (21)$$

The other part of $I_y(t)$ (i.e., the irrelevant component) will be called $I_2(t)$, so that

$$I_y(t) = \mathcal{P} I_y(t) + (1 - \mathcal{P})I_y(t) = I_1(t) + I_2(t). \quad (22)$$

As shown by Zwanzig,[9] the above equations imply in a straightforward manner that $I_1(t)$ satisfies the following integro-differential equation:

$$\frac{\partial I_1(t)}{\partial t} = \mathcal{P} i \mathcal{L}(t_c)\left\{I_1(t) + \int_0^t dt' \exp[(t - t')(1 - \mathcal{P}) i \mathcal{L}(t_c)]\right.$$
$$\left. \times (1 - \mathcal{P}) i \mathcal{L}(t_c) I_1(t')\right\}, \quad (23)$$

where the fact that $(1 - \mathcal{P}) I_y(0) = 0$ has been used to eliminate a term which would otherwise appear.

Now notice that

$$\mathcal{P} \mathcal{L}(t_c) I_1(t) = \mathcal{P} \mathcal{L}(t_c) I_y \langle I_y^2\rangle^{-1} G(t)$$
$$= \mathrm{Tr}\{I_y [\mathcal{3C}_e(t_c), I_y]\} \langle I_y^2\rangle^{-2} G(t) I_y,$$

which vanishes because the trace is invariant to cyclic permutation. Thus the first term on the right-hand side of Eq. (23) is zero. If we now multiply both sides of Eq. (23) by I_y and take the trace, we obtain

$$\frac{\partial G(t)}{\partial t} = - \int_0^t dt' \langle I_y^2\rangle^{-1} \langle I_y \mathcal{L}(t_c)$$
$$\times \exp[(t - t')(1 - \mathcal{P}) i\mathcal{L}(t_c)] \mathcal{L}(t_c) I_y\rangle G(t'), \quad (24)$$

which is an exact integro-differential equation for $G(t)$. If this equation can be solved, formally or otherwise, then an exact equation for $\langle I_y(nt_c)\rangle$ can be obtained immediately by setting $t = nt_c$. Thus, Eq. (24) completely determines the evolution of the transverse magnetization at the end of the nth-pulse cycle.

III. APPLICATION TO OSTROFF-WAUGH EXPERIMENT

In this section we shall apply the preceding results to analyze the Ostroff-Waugh experiment[1] for

production of multiple dipolar echoes in solids containing only a single spin species.[2,6] Further applications to the case of several spin species and to other pulse sequences designed to accomplish high-resolution NMR in solids will be discussed in a subsequent publication. For the case considered here, we will rederive the short-time result of Waugh and Wang from Eq. (24), and will show as well that under certain conditions this equation simplifies to imply an exponential decay of the magnetization at long times. When this is the case, an explicit but formal expression for the decay time T^* is automatically obtained. The resulting dependence of T^* upon t_c (or τ) can be quite varied depending upon the circumstances; we discuss briefly the manner in which different τ dependences may arise.

1. *Specialization to the P_x, τ, P_y, $(2\tau, P_y)_n$ pulse cycle*. The one-cycle propagator corresponding to the Ostroff-Waugh pulse sequence is[4]

$$L(t_c) = \exp(-i\mathcal{K}_d\tau)\exp(-2i\tilde{\mathcal{K}}_d\tau)\exp(-i\mathcal{K}_d\tau) ,$$

(25)

where $t_c = 4\tau$, $\tilde{\mathcal{K}}_d = P_y\mathcal{K}_d P_y^{-1}$, and $\mathcal{K}_d$ is the truncated dipolar Hamiltonian appropriate to solids:

$$\mathcal{K}_d = \sum_{i<j} \gamma^2\hbar r_{ij}^{-3} P_2(\cos\theta_{ij})(\vec{I}_i \cdot \vec{I}_j - 3I_{iz}I_{jz}) .$$

(26)

For simplicity, we consider the case in which the internal Hamiltonian contains only dipole-dipole interactions, but scalar couplings can be trivially included if desired; nothing essential is changed.

Since the one-cycle propagator given in Eq. (25) is symmetrical [i. e., $L^\dagger(t_c) = L(-t_c)$], all the odd-order correction terms in Eq. (16) vanish (see Appendix). Therefore,

$$L(t_c) = \exp[-it_c\mathcal{K}_e(t_c)] ,$$

(27)

where

$$\mathcal{K}_e(t_c) = \overline{\mathcal{K}} + \sum_{k=1}^\infty t_c^{2k} F_{2k} \equiv \overline{\mathcal{K}} + V(t_c) .$$

(28)

The first two nonvanishing terms in Eq. (28) involve the quantities $\overline{\mathcal{K}}$ and F_2, which are given by

$$\overline{\mathcal{K}} = \tfrac{1}{4}iL_1 = \tfrac{1}{2}(\mathcal{K}_d + \tilde{\mathcal{K}}_d) ,$$

$$F_2 = (i/4^3)[L_3 - (1/3!)L_1^3] ,$$

where L_k is the coefficient of τ^k in a power-series expansion of $L(4\tau)$ [Eq. (27)].

So far we have not questioned the convergence of the Magnus expansion in Eqs. (16) and (28). The expansion is certainly expected to converge rapidly if t_c is small enough, but in practice this may not always be the case. In any event, we shall consider $V(t_c)$ to be defined by $\mathcal{K}_e(t_c) - \overline{\mathcal{K}}$, whether or not the expansion in Eq. (28) is convergent.

We next note that $[\overline{\mathcal{K}}, I_y] = 0$, which in turn immediately implies that $\wp[\overline{\mathcal{K}}, A] = 0$ for any operator A. Making use of these facts and Eq. (28), we finally

obtain

$$\frac{\partial G(t)}{\partial t} = -\int_0^t dt'\, K(t'|t_c) G(t - t') ,$$

(29)

where

$$K(t'|t_c) = \langle I_y^2\rangle^{-1}\langle I_y\mathcal{L}'(t_c)$$

$$\times \exp[i\mathcal{L}_0 t' + i(1 - \wp)\mathcal{L}'(t_c)t']\mathcal{L}'(t_c)I_y\rangle , \quad (30)$$

$\mathcal{L}_0 A \equiv [\overline{\mathcal{K}}, A]$, and $\mathcal{L}'(t_c)A \equiv [V(t_c), A]$ for any operator A. Equations (29) and (30) completely determine the evolution of the magnetization, and are valid for both short and long times. These equations are closely analogous to Terwiel and Mazur's expressions for the spin-spin relaxation function.[20] The quantities $\overline{\mathcal{K}}$ and $V(t_c)$ of the present case play, respectively, the roles of secular and nonsecular Hamiltonians. Of course, the nonsecular perturbation in the present case is introduced by the fact that the characteristic repetition period t_c is finite. If $t_c \ll T_2$, the nonsecular effects become negligibly small and the motion of the system can be described in terms of the average Hamiltonian $\overline{\mathcal{K}}$. In this case the magnetization will be locked along the y direction of the rotating frame[4]; i. e., there will be no decay of the echo envelope. This situation is of course similar to the familiar "motional narrowing" effect, as has been discussed by Haeberlen and Waugh. [13]

2. *Behavior at short times*. We wish here to show that the above results reduce for short times to the results of Waugh and Wang.[4] For small τ we have, from Eq. (28),

$$V(t_c) = t_c^2 F_2 + O(t_c^4)$$

$$= \tfrac{1}{4}i\tau^2[L_3 - (1/3!)L_1^3] + O(\tau^4) , \quad (31)$$

and we obtain for short times and small τ, from Eq. (30),

$$K(t'|t_c) = t_c^4\langle I_y[F_2, [F_2, I_y]]\rangle\langle I_y^2\rangle^{-1} + O(t_c^6)$$

or

$$K(t'|\tau) = (i^2/4^2)\tau^4\langle I_y[L_3, [L_3, I_y]]\rangle\langle I_y^2\rangle^{-1} .$$

In terms of the brace notation of Waugh and Wang,[4] this equation becomes

$$K(t'|\tau) = (i^2/4^2)\tau^4[L_3^2]/[1] .$$

(32)

Substituting Eq. (32) into Eq. (29), solving for $G(t)$ to lowest order in t, and setting $t = nt_c = 4n\tau$, we obtain

$$\langle I_y(nt_c)\rangle = \langle I_y(4n\tau)\rangle = [1 + \tfrac{1}{2}n^2\tau^6 L_3^2 + \cdots] ,$$

(33)

which is identical to Eq. (41) of Waugh and Wang. [21]

3. *Behavior at long times*. We now wish to examine the implications of our basic equations (29) and (30) for long times, i. e., for $nt_c \gg T_2$. To do so, we observe that while the decay function $G(t)$ decays slowly to zero on a time scale $T_{1\rho}$, the kernel

$K(t' \mid t_c)$ [which consists essentially of the time autocorrelation function of the quantity $\mathcal{L}'(t_c)I_y$, with a modified propagator] is expected to decay rapidly to zero in a time of the order of T_2.[22] If this is the case, then for $T_2 \ll nt_c \ll T_{1\rho}$, one may approximate Eq. (29) by setting the upper integra-

tion limit equal to ∞ and replacing $G(t-t')$ by $G(t)$. When this approximation is made, the function $G(t)$ (and hence the magnetization) assumes an exponential decay, which in fact is what is observed experimentally at long times. The time constant T^* associated with the decay is then given by

$$\frac{1}{T^*} = -\int_0^\infty dt' \; \frac{\langle [\mathcal{L}'(t_c)I_y] \exp[i\mathcal{L}_0 t' + i(1-\wp)\mathcal{L}'(t_c)t'][\mathcal{L}'(t_c)I_y] \rangle}{\langle I_y^2 \rangle} \;, \tag{34}$$

where, in spite of the minus sign, $1/T^*$ must of course be positive. It is perhaps more revealing to write $1/T^*$ as

$$\frac{1}{T^*} = -\frac{\langle [\mathcal{L}'(t_c)I_y]^2 \rangle}{\langle I_y^2 \rangle} \, \tau_c(t_c) \;, \tag{35}$$

where the characteristic correlation time $\tau_c(t_c)$ associated with the decay of the kernel is given by

$$\tau_c(t_c) = \int_0^\infty dt' \; \frac{\langle [\mathcal{L}'(t_c)I_y] \exp[i\mathcal{L}_0 t' + i(1-\wp)\mathcal{L}'(t_c)t'][\mathcal{L}'(t_c)I_y] \rangle}{\langle [\mathcal{L}'(t_c)I_y]^2 \rangle} \;. \tag{36}$$

Equation (34) [or Eqs. (35) and (36)] must contain the full dependence of T^* upon t_c, although the precise nature of this dependence has yet to be extracted from the formalism. Let us therefore go on to consider particular circumstances and the t_c dependence which arises in each.

In the limit of small t_c $(t_c \ll T_2)$, it is reasonable to suppose that Eq. (34) reduces to

$$1/T^* = -t_c^4 \langle I_y^2 \rangle^{-1} \int_0^\infty dt' \, \langle [F_2, I_y] \exp(i\mathcal{L}_0 t')[F_2, I_y] \rangle \;. \tag{37}$$

We emphasize, however, that in order to obtain Eq. (37) from Eq. (34) in the limit $t_c/T_2 \to 0$ it is necessary to interchange limiting operations in a manner which has not been mathematically justified.[23] Equation (37) bears an obvious resemblance to the well-known expressions for the ordinary spin-lattice and spin-spin relaxation times T_1 and T_2.[24] Note that according to Eq. (37) $1/T^*$ should be proportional to t_c^4 (or τ^4) for small t_c. This result is in disagreement with experimental results for CaF$_2$, which show a proportionality between T^* and t_c^{-5}, although it may account for the departure from this relationship in the case of K$_2$SiF$_6$ at small t_c.

In practice, however, the mathematical limit $t_c/T_2 \to 0$ is never achieved, and we must consider the question of how to include correction terms in Eq. (37) arising from the fact that t_c is finite. The simplest way to do this is to *assume* that it is legitimate to express $1/T^*$ as a power series in t_c. This expansion can be generated in a straightforward manner from the basic expression (34) for $1/T^*$. One first expands the exponential operator in powers of $\mathcal{L}'(t_c)$, allowing, of course, for the fact that the operators in the exponent do not nec-

essarily commute. One then expands $\mathcal{L}'(t_c)$, wherever it appears, in powers of t_c; since $\mathcal{L}'(t_c)A = [V(t_c), A]$, this expansion is essentially the same as that in Eq. (28). But since only even powers of t_c appear in Eq. (28), it is clear that only even powers can appear in $1/T^*$ as well. That is, *if* $1/T^*$ may be expanded in powers of t_c, then the expansion begins with a term of order t_c^4, and only even powers of t_c appear:

$$1/T^* = a_1 t_c^4 + a_2 t_c^6 + a_3 t_c^8 + \cdots \;, \tag{38}$$

where a_1 is of course just the negative of the integral appearing in Eq. (37).

But there is a serious difficulty with this power-series approach, for experimentally it is found in several cases that $1/T^*$ is proportional to t_c^5. According to Eq. (38), $1/T^*$ should start out proportional to t_c^4, and even if the t_c^4 term should happen to be zero, the next term would be proportional to t_c^6 rather than t_c^5. One possible explanation for this disagreement is the following. Suppose it turns out that, although the t_c^4 and t_c^6 terms in Eq. (38) are important, all higher-order terms are negligible in the range of t_c considered. Then Eq. (38) may be rewritten in the form

$$1/T^* = t_c^5 (a_1/t_c + a_2 t_c) \;. \tag{39}$$

If we suppose further that $a_1 \approx a_2 t_c^2$ in the range of t_c considered, then we see from Eq. (39) that it is possible for the combination of a t_c^4 term and a t_c^6 term to simulate the behavior of t_c^5 over a reasonably wide range of t_c. Of course, this argument is purely conjectural; it rests upon the above suppositions concerning the relative magnitudes of the coefficients a_k in Eq. (38). In order to justify this interpretation, it would be necessary to evaluate
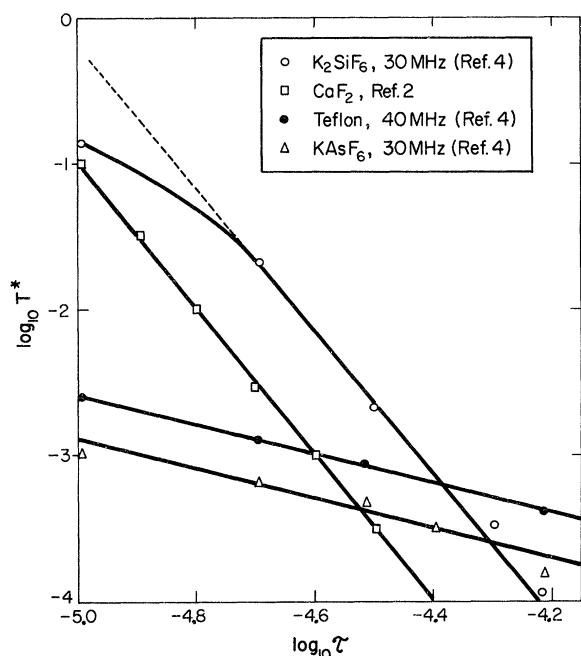
FIG. 1. Dependence of the decay time T^* on pulse spacing τ ($\tau = t_c/4$; t_c is the cycle time) in K_2SiF_6, CaF_2, $KAsF_6$, and Teflon. These data were obtained from Figs. 2 and 3 of Ref. 4. Note that $T^* \propto \tau^{-5}$ for CaF_2 and K_2SiF_6, while $T^* \propto \tau^{-1}$ for $KAsF_6$ and Teflon.

the quantities a_k; this is unfortunately a prohibitive task. Besides, even if this explanation is correct for CaF_2 and K_2SiF_6 its applicability is in no sense general, for there are several other compounds which show other dependences of T^* upon t_c (see Fig. 1). In particular, for Teflon and $KAsF_6$ one finds a proportionality between $1/T^*$ and t_c; there is no apparent way to reconcile these observations with Eq. (38).

The above difficulties suggest that it simply may not be permissible to express $1/T^*$ as a power series in t_c, at least in the experimentally accessible range of t_c. This may occur because experimentally t_c is not made small enough for the series to converge rapidly or at all, or it may be due to some inherent nonanalyticity in the problem. That is to say, $1/T^*$ may simply not be an analytic function of t_c over an interval containing $t_c = 0$. But if the power-series expansion of $1/T^*$ is not legitimate, then it becomes apparent that $1/T^*$ may exhibit practically any t_c dependence that one can imagine. In particular, the proportionality between $1/T^*$ and t_c^5 which is observed for CaF_2 and K_2SiF_6 may arise in the following manner. Let us first suppose that t_c is small enough for the Magnus expansion (28) to converge, which is almost certainly the case. However, the fact that experimentally $t_c \lesssim T_2$ (instead of the more favorable condition $t_c \ll T_2$) means that we cannot expect to be able to

truncate the expansion at any low order. If we now expand $\mathcal{L}'(t_c)$ in powers of t_c *everywhere except in the exponential*, Eq. (34) becomes

$$\frac{1}{T^*} = -t_c^4 \int_0^\infty dt' \; \frac{\langle M_2 E(t' \mid t_c) M_2 \rangle}{\langle I_y^2 \rangle}$$

$$-t_c^6 \int_0^\infty dt' \; \frac{\langle M_4 E(t' \mid t_c) M_2 + M_2 E(t' \mid t_c) M_4 \rangle}{\langle I_y^2 \rangle} + \cdots ,$$

$$(40)$$

where $M_k \equiv [F_k, I_y]$ and $E(t' \mid t_c) \equiv \exp[i\mathcal{L}_0 t' + i(1 - \varphi) \times \mathcal{L}'(t_c) t']$. In obtaining Eq. (40) from Eq. (34) we have effectively assumed that the difficulty in expressing $1/T^*$ as a power series in t_c is associated with the exponential operator rather than the rest of the expression.

As mentioned, we cannot expect to be able to truncate Eq. (40) at any low order on the basis of the smallness of t_c. However, it is reasonable physically to assume that the progressively higher-order correlation functions which occur in succeeding terms of Eq. (40) decay to zero with increasing rapidity.[8] If this is the case, then we can truncate the expansion in Eq. (40) on this basis regardless of the fact that $t_c \lesssim T_2$. We then obtain

$$1/T^* = -(\langle M_2^2 \rangle / \langle I_y^2 \rangle) t_c^4 \tau_c^0(t_c) , \qquad (41)$$

where $\tau_c^0(t_c)$ is given by

$$\tau_c^0(t_c) = \int_0^\infty dt' \; \frac{\langle M_2 E(t' \mid t_c) M_2 \rangle}{\langle M_2^2 \rangle} \qquad (42)$$

and is presumed not to be expressible as a power series in t_c. We see from Eq. (41) that if $1/T^*$ is to be proportional to t_c^5 then $\tau_c^0(t_c)$ must simply be proportional to t_c. This will occur if the integrand of Eq. (42) [which is the time autocorrelation function of the operator M_2, taken with the modified propagator $E(t' \mid t_c)$ and normalized to unity at $t' = 0$] is flat up to a time $t' = \alpha t_c$ (where α is a constant), beyond which it assumes a very rapid decay. (Actually, all that is necessary is that the area be equal to αt_c, but this is perhaps less easily imagined.) Then $\tau_c^0(t_c) \approx \alpha t_c$ and one obtains

$$1/T^* = -\alpha (\langle M_2^2 \rangle / \langle I_y^2 \rangle) t_c^5 . \qquad (43)$$

If α is set equal to unity, we obtain the earlier result of Waugh and Wang,[4] obtained by use of a *Stosszahlansatz*.

The proportionality between $1/T^*$ and t_c which is observed for Teflon and $KAsF_6$ may be interpreted in the same manner. In order for Eq. (41) to imply that $1/T^*$ is proportional to t_c, it is necessary for $\tau_c^0(t_c)$ to be proportional to t_c^{-3}. The corresponding behavior of the correlation function in the integrand of Eq. (42) may readily be imagined.[25] If, for example, this correlation function decays exponentially with a time constant proportional to t_c^{-3} then $\tau_c^0(t_c)$ is, of course, proportional to t_c^{-3}.

This is a sufficient condition but certainly not a necessary one.

IV. CONCLUSION

We have seen that a theory of the decay of transverse spin magnetization in multiple-pulse NMR experiments can be formulated in close analogy to theories of more conventional relaxation experiments. In particular, our treatment makes clear the close connection which exists between the limit $(t_c \to 0, n \to \infty, nt_c = t = \text{const})$ in multiple-pulse NMR and the familiar weak-coupling limit of statisical mechanics.[9]

We then focused attention on the Ostroff–Waugh experiment for producing multiple spin echoes in dipolar solids, and obtained a formal expression for the decay time T^* which in principle contains the full dependence of this quantity upon the pulse spacing τ. Guided by available experimental data, we gave a discussion of the different possible dependences of T^* upon τ which may arise in different circumstances. In order to obtain agreement with experiment, the correlation function which determines T^* [see Eq. (34)] must apparently manifest different types of unusual behavior in different samples. However, experimental data of this type are very scarce (to our knowledge, Fig. 1 is a complete summary of such data for samples containing a single spin species). Further measurements of the dependence of T^* upon τ, both for the Ostroff–Waugh experiment and for other pulse sequences, would be very helpful in the resolution of the questions we have raised. We hope that this work will serve as a stimulus for further experi-

mental investigations of the dependence of T^* upon the pulse spacing.

APPENDIX

For convenience we rewrite here Eqs. (15) and (16):

$$L(t_c) = \exp[-it_c \mathcal{3C}_\theta(t_c)] , \qquad (A1)$$

$$\mathcal{3C}_\theta(t_c) = \overline{\mathcal{3C}} + \sum_{k=1}^{\infty} t_c^k F_k , \qquad (A2)$$

where the fact that $\overline{\mathcal{3C}}^{(k)}(t_c) = t_c^k F_k$ has been used. Since $L(t_c)$ is a unitary operator, it follows that

$$L^\dagger(t_c) = L^{-1}(t_c) = \exp[it_c \mathcal{3C}_\theta(t_c)] . \qquad (A3)$$

If $L(t_c)$ is *symmetrical* as well, that is, if

$$L^\dagger(t_c) = L(-t_c) , \qquad (A4)$$

then one also has

$$\exp[it_c \mathcal{3C}_\theta(t_c)] = \exp[it_c \mathcal{3C}_\theta(-t_c)] . \qquad (A5)$$

Therefore,

$$\mathcal{3C}_\theta(t_c) = \mathcal{3C}_\theta(-t_c) \qquad (A6)$$

or, from Eq. (A2),

$$\sum_{k=1}^{\infty} t_c^k F_k = \sum_{k=1}^{\infty} (-t_c)^k F_k . \qquad (A7)$$

Therefore, F_k must be equal to zero if k is odd.

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[22]A rigorous demonstration that $K(t' \mid t_c)$ decays rapidly would be prohibitively difficult because of the high-order correlations involved. However, this rapid decay is plausible on the basis of the similarity in structure between $K(t' \mid t_c)$ and the correlation function associated with T_2 processes in solids. In addition, if one expands $K(t' \mid t_c)$ in powers of t' then it is found that the lowest-order contribution to the coefficient of $(t')^k$ is a modified kth moment of a type which is frequently taken in the

literature [see Refs. 4, 13, and 19(b)] to be of the order of T_2^{-k}. This indicates that the relevant time parameter is t'/T_2, i.e., that the decay of $K(t' \mid t_c)$ takes place on a time scale T_2. But regardless of these qualitative arguments, the rapid decay of $K(t' \mid t_c)$ is necessary in order that the decay of $G(t)$ be exponential, as observed experimentally.

[23]Both the infinite sum which defines the exponential operator and the infinite integral are associated with limiting processes, so the passage from Eq. (34) to Eq. (37) in the limit as $t_c/T_2 \to 0$ is by no means as obvious as it may at first appear. See Ref. 20 for a related discussion.

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[25]One might wonder whether the inclusion of lattice motion in the theory would be capable of explaining a proportionality between $1/T^*$ and t_c. We have made some preliminary calculations of this type, and find that the inclusion of lattice motion does not appear to alter the situation materially. In particular, the leading term in a power-series expansion of $1/T^*$ is still proportional to t_c^4, just as in the present case [see Eq. (38)].

Proton Nuclear Magnetic Relaxation in Antiferromagnetic NiCl₂·6H₂O, CoCl₂·6H₂O, CuCl₂·2H₂O, and MnBr₂·4H₂O[†][*]

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Proton-spin-lattice relaxation times (T_1) were measured by us in antiferromagnetic NiCl₂·6H₂O $(T_N = 5.34\,°K)$, CoCl₂·6H₂O $(T_N = 2.29\,°K)$, and MnBr₂·4H₂O $(T_N = 2.13\,°K)$ in the temperature range $4.18 - 1.12\,°K$. Spin-echo experiments were also carried out over the same temperature range to determine the homogeneous transverse relaxation time T_2 in NiCl₂·6H₂O and the extent of the inhomogeneous broadening in CoCl₂·6H₂O. Samples of various impurities and shapes were investigated. The spin-lattice relaxation time T_1 was found to be strongly temperature dependent for the first two crystals. The T_1 data from the CoCl₂·6H₂O crystals could be fit to a power law $(T_1 \propto T^{-7})$, but the T_1 data from the NiCl₂·6H₂O crystals could not. The temperature dependence of T_1 for MnBr₂·4H₂O was not determined because of the short temperature range over which we were able to make measurements. The temperature dependence of T_1 for the first two crystals along with the experimental results for CuCl₂·2H₂O $(T_N = 4.3\,°K)$ have been explained through a first-order two-magnon process plus a second-order three-magnon process. The second-order three-magnon process arises from the four-magnon exchange interaction which has been shown by Beeman and Pincus to completely supersede the first-order three-magnon process when $T > T_{AE}$. The impurity levels, the sample shape, and the orientation of an external magnetic field H_0 had no effect on the temperature dependence of T_1. In NiCl₂·6H₂O the value of T_2 measured from a 90°-90°-pulse-sequence experiment increased from a value of about 28 μsec at 4.18 °K to a value of about 65 μsec at 2.3 °K and then at 2.1 °K dropped to about 30 μsec and stayed at this value down to 1.12 °K. In CoCl₂·6H₂O the inhomogeneous broadening was dependent on the orientation of H_0 and the sample shape. An rf enhancement was found in CoCl₂·6H₂O for H_0 along the anisotropy axis (c axis).

I. INTRODUCTION

The first experimental measurements of the spin-lattice relaxation time T_1 for protons in antiferromagnetic materials were made by Hardeman et al.[1] Moriya[2] and Van Kranendonk and Bloom[3] tried to explain the dependence of T_1 on the absolute temperature T using a relaxation process due to the Raman scattering of magnons. Their results were of the right order of magnitude, but the temperature dependence was slower than the T^{-7} dependence found experimentally. Pincus and Winter[4] then proposed a theory which gave the T^{-7} temperature dependence but required $T \ll T_{AE}$, where $k_B T_{AE} = \hbar \omega_{AE}$ and $\hbar \omega_{AE}$ is the magnon energy

gap. They assumed that the magnetostrictive terms in the Hamiltonian produced a magnon component in the thermal phonon spectrum allowing the phonons to participate directly in the relaxation processes. The T^{-7} temperature dependence in CuCl₂·2H₂O $(T_{AE} \simeq 1.4\,°K)$ covers the range $T > T_{AE}$ as well as the range $T < T_{AE}$. Other crystals, CoCl₂·6H₂O $(T_{AE} \simeq 2\,°K)$ and KMnF₃ $(T_{AE} \simeq 0.3\,°K)$, that have also exhibited this temperature dependence for T_1 have also included the range $T > T_{AE}$. In fact for KMnF₃ the middle of the temperature range is on the order of 100 times T_{AE}. Also, as is reported in Sec. IV, the temperature dependence of T_1 in NiCl₂·6H₂O cannot be fitted by a power law. Additional arguments and evidence against